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Vol. 28. No. 226. October 1942.

THE SEPARATION OF GASES.

By Dr. Martin Ruhemann.

Scope of Gas Separation.

The properties of most gases, whether natural or artificial, have had a profound influence not only on the history of technology, with consequent repercussions on human society, but on the evolution of plant and animal life, including man himself. Clearly a different composition of the earth's atmosphere would have led to very different organic forms and might have given rise to something very different from the human race. The atmosphere, with its unvarying composition, is now the basis of vast technological processes of which blast furnaces are but one, though perhaps the most outstanding example. The radical differences between the British and the American gas industries is due to the fact that the gas industry in America is based primarily on natural gas, consisting mainly of methane, while that in Britain is based on retort gas with a very different and far more complex composition.

Nature has her own way of separating gaseous mixtures. Thus, when producer gas is burned, the molecules of oxygen in the air select the hydrogen and carbon monoxide in the gas and enter into the well-known reactions, leaving the uncombustible nitrogen. In many cases we have so perfectly adapted our technique to this state of affairs that we are inclined to look down the wrong end of the telescope and insist that the chance composition of some of our natural and technological gases has been ordained by Providence to suit human needs. On the other hand, in an increasing number of cases we have been forced to admit the pernicious influence of certain constituents in gaseous mixtures and to take the necessary steps to remove them. The presence of sulphur compounds in town's gas is an example and, in more recent times, the removal of carbon monoxide from the initial reagents of the synthetic ammonia process has become a necessity, owing to its ruinous effect on the catalysts. Nowadays there is a marked tendency to get away from the chance composition of gaseous mixtures, to produce from them pure or almost pure gases or to make up mixtures of a definite composition particularly suitable for technological processes. A gas-separating industry has developed, as a result of which the presence of certain constituents together in a gaseous mixture is no longer a valid reason for their joint utilisation.

The significance of this statement is best realized by considering the quantities and compositions of the gases surrounding us. Take as a first example atmospheric air. It is present in virtually unlimited quantities. Apart from its main constituents, it contains relatively small, but still enormous amounts of the so-called rare gases. Every one of its components is useful and most are in constant use—oxygen for cutting and welding, nitrogen for fertilizers and explosives, argon for incandescent bulbs and neon for discharge tubes. Shortly before the war krypton and xenon, present in a concentration of one in a million, were being used for

lamps, and the only reason why helium was not being separated from air was that it could be obtained more cheaply from other sources. It is important to realize that all these developments have taken place in the present century, mainly as the result of Linde's invention of a machine for producing liquid air on a commercial scale.

Most of the other common gases contain combustible components and are connected in some way with the transformations of organic matter. Some are associated with coal and its treatment; others are associated with mineral oils. The utilization of most of these gases is to-day still at a primitive stage, in that most of them are either burned or wasted, in spite of the fact that they contain a great variety of constituents, some of which are valuable and admirably suited for important chemical processes. Though the science of gas separation is highly developed, its industrial application is still new and has many technical, psychological, and economic difficulties to overcome. At the same time, marked progress has already been made in the economic utilization of some of these mixtures, especially coke-oven gas and the gases evolved in the processes of cracking and pyrolysis.

TABLE I.

Gases Associated with Coal.

	Compositions in % by volume.					
	CH_4.	C_nH_m.	H_2.	CO.	CO_2.	N_2.
Town's gas . . .	33	3	56	8	—	—
Coke-oven gas . .	30	3	50	7	2	8
Low-temperature gas .	48	13	27	7	3	2
Firedamp . . .	97	—	—	—	2	1
Produced gas . .	3	—	12	28	3	54
Mond gas . . .	4	—	25	12	16	43
Water gas . . .	1	—	49	42	5	3

TABLE II.

Gases Associated with Oil.

	Compositions in % by volume.								
	H_2.	CH_4.	C_2H_6.	C_3H_8.	C_4H_{10}.	C_2H_4.	C_3H_6.	C_4H_8.	N_2.
Natural gas	—	99·8	—	—	—	—	—	—	—
	—	95	—	—	—	—	—	—	2
	—	81	11	6	2	—	—	—	—
	—	41	—	—	—	—	—	—	59
(contains 2% He)	—	15	—	—	—	—	—	—	83
Cracker gas	6	31	15	5	1	22	14	6	—
Pyrolysis gas	19	43	8	6	1	18	4	1	—

In the Tables I and II some typical figures are given for the compositions of the best known of these gases. The compositions vary considerably and the figures shown are to be regarded only as examples. They show the basic characteristics of the several types: the presence of hydrogen

in all the " artificial " gases, the varying concentrations of carbon monoxide in gases produced from coal, the predominance of methane in fire-damp and natural gas, and the olefine content of the products of cracking and pyrolysis.

Another gas should be added to this list, as it is becoming increasingly available for industrial purposes, and that is the mixture of 70 per cent. methane and 30 per cent. carbon dioxide obtained in the decomposition of sewage. In the modern sewage works of Birmingham and West Middlesex, gas from sewage sludge is being utilized as engine fuel, and the modernization of the whole sewage-disposal system in this and other countries will furnish large quantities of this valuable mixture.

It is difficult to obtain accurate data on the quantities of these gases which are annually produced or emerge from the earth's surface. About 3×10^{12} cu. ft. of natural gas are utilized every year, over 90 per cent. in the United States. Much larger quantities are wasted. The annual production of coke-oven gas for the whole world is about the same. Town's gas is produced in smaller quantities, and only in our own country is more gas made as towns' gas in retorts than as coke-oven gas in ovens. The amount of cracker gas produced is about one-tenth of this figure.

Until recently only very small portions of these gases were separated; but the gas-separating industry has been growing rapidly, and it seems reasonable to suppose that, within a few years, the amounts of some of the gases separated will be a considerable proportion of the quantities produced. One installation built some years ago in the Soviet Union separated rather more than 10^{10} cu. ft. of coke-oven gas per annum, probably not far short of 1 per cent. of the total amount of coke-oven gas produced in the world. If all the major countries were to erect plant of this size, separation of coke-oven gas would soon catch up with production.

The time is not far distant when the economic utilization of the world's gas resources will become an urgent problem. The quantities of hydrogen, carbon monoxide, and olefines required for chemical processes will be so great that we shall no longer be in a position to squander these gases by firing them together with any other constituents that may occur in mixtures. Then the separation of gases will become the rule instead of the exception.

Methods of Gas Separation.

Since all gases are completely miscible, the separation of gaseous mixtures necessitates the introduction of other phases that are not gaseous. This can be achieved either by introducing liquid or solid absorbents or by a partial liquefaction of the initial mixture. In general the latter method is the more economical.

The critical temperatures of most gases in natural and industrial mixtures are below the temperature of the environment. Separation by partial liquefaction therefore requires low temperatures, which necessitates a specialized technique and the employment of refrigerating machinery. Even if the ultimate products are to be withdrawn at atmospheric temperature, refrigeration is still required to cool down the mixture initially and to maintain the low temperature in the plant during the separating process, by absorbing heat inflow from without and heat exchanged within

the units. If, as in the case of the liquid oxygen industry, one or more products must be withdrawn as cold liquids, a much greater refrigerating performance is needed, so that, especially in large plants, power becomes the principal item in the production costs. Hitherto refrigeration at the very low temperatures involved in gas separation has always been achieved with compression plant in which the power consumption is considerable.

Cooling can be effected in either of two ways : by introducing foreign refrigerants or by utilizing the gaseous mixtures themselves or some of their fractions as refrigerating agents. Both methods are used extensively in industrial practice, frequently in the same plant. Thus in the classical Linde plant for separating air and producing liquid or gaseous oxygen the compressed air is the main refrigerant, but is supplemented by an auxiliary closed system containing ammonia. Most Russian plants for separating cracker gas use two auxiliary cycles, one with ammonia and one with ethylene, whereas a number of American plants for the same purpose make use of the refrigerating capacity of the components of the cracker gas.

When a gas that is to be separated serves as its own refrigerant, the customary distinction between the refrigerant and the substance to be cooled becomes somewhat obscure. In the course of its passage through the plant, the mixture divides into one portion which is cooled and separated and another which merely acts as a refrigerant. This is a feature of most plants for separating air.

The use of the so-called permanent gases as refrigerants is necessary, but, in current practice, not very efficient. This is because the gases are merely compressed and expanded in valves without previous liquefaction. The refrigerating capacity of a compressed gas is very much smaller than that of an evaporating liquid and the process is more irreversible. Thus a given refrigerating performance requires more power than when the refrigerant is liquefied before expansion.

There are two ways of overcoming this difficulty. One is to allow the compressed gas to do work during expansion, thus increasing the refrigerating performance by the thermal equivalent of the power generated. This may be achieved with a reciprocating expansion engine or a turbine. Until recently only expansion engines were used for this purpose, as introduced by Claude at the beginning of the century and later developed by Heylandt. These expansion engines, which operate between 1 and 200 atm., are only moderately efficient and not easy to handle. Lubrication at low temperatures is a serious difficulty, and care must be taken to avoid liquefaction in the expansion cylinder. In the Heylandt plant, which was until recently the most efficient machine for producing liquid oxygen, the compressed air is separated into two almost equal streams; one is expanded in the engine from room temperature to about — 130° C., while the other is pre-cooled in a heat exchanger and subsequently expanded in a valve as in the Linde system. The air passed through the expansion engine thus serves as a refrigerant for the rest of the air, which also acts as its own refrigerant. This combination was found to be the most efficient, as it avoids expansion in the cylinder at very low temperatures. On the other hand, it requires higher pressures than the original Claude plant.

In the " rich air " industry, which produces impure oxygen for blast

furnaces, the Linde–Fränkl system has for some time employed expansion turbines at temperatures close to atmospheric and pressures of about 3 atm. abs. as an auxiliary source of cooling. The use of turbines as primary sources of refrigeration for air at low temperatures has been delayed through technical difficulties. This problem was solved quite

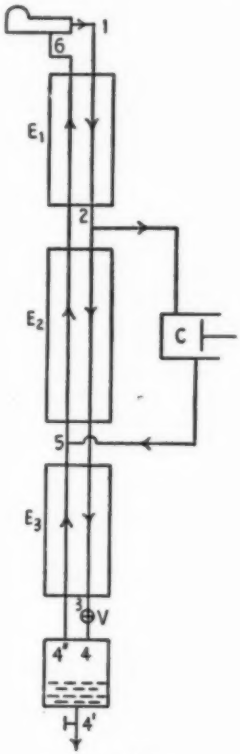


FIG. 1.*

CLAUDE LIQUEFIER.

recently by Kapitza in Moscow, who designed an expansion turbine working from 7 atm. at very low temperatures, taking into account the fact that, under these conditions, air is about midway between a gas and a liquid in the usual sense. It appears that Kapitza's machine can produce cheaper " rich air " than the Linde–Fränkl plant. It was intended mainly to supply impure oxygen for the underground gasification of coal and will, incidentally, yield large quantities of krypton and xenon for filling incandescent bulbs. The change-over from argon to a krypton–xenon

* Blocks kindly lent by the Institution of Chemical Engineers.

mixture in bulbs has been calculated to save several million kilowatt-hours per annum.

The other method of improving the refrigerating performance of gas-separating plant is based on the so-called cascade principle. It is possible to secure liquefaction of compressed gases before expansion, and a consequent rise in efficiency, by employing a series of refrigerants with different critical temperatures and allowing each compressed gas to condense in the evaporating liquid of a gas with a higher critical point. Thus, by using four cycles containing ammonia, ethylene, methane, and air respectively, each gas being liquefied before expansion, the liquefaction of air and its separation into oxygen and nitrogen can be effected and the separated oxygen removed as a cold liquid with a smaller expenditure of mechanical work than by any other method. The cascade principle,

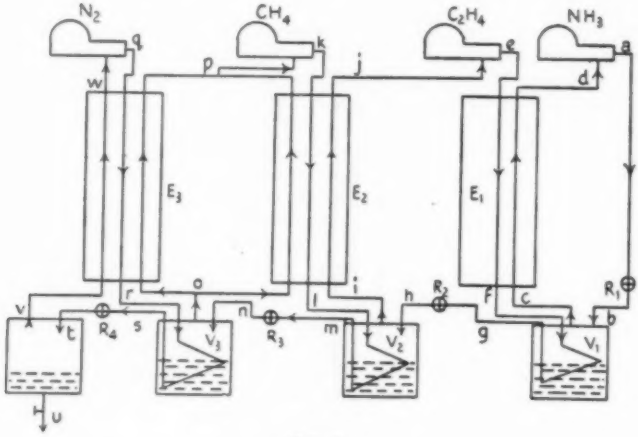


FIG. 2.

KEESOM'S NITROGEN CASCADE.

though conceived by Pictet over half a century ago and utilised in the Leyden laboratory by Kamerlingh-Onnes, has never yet been employed in large-scale industrial practice. However, with the present tendency towards larger plant and liquid products and the consequent importance of power economy, this method will probably soon find its place in industry.

A further probable development in power economy will be the increased use of absorption methods. Hitherto absorption units with ammonia-water mixtures have been used mainly at relatively high temperatures. By using heat, especially waste steam, instead of power, they can be made very economical. The work of Altenkirch in Germany and of the late Dr. Maiuri in England has shown theoretically and practically the value of the absorption method. Dr. Maiuri devoted much time in the later years of his life to developing the method for lower temperatures, and it is to be hoped that this work will bear fruit in the near future.

The separation of a gaseous mixture into two phases by partial liquefaction is in general a first step towards the separation of the components in concentrating one of the constituents in the liquid or the gaseous phase. In some cases this is sufficient to effect practically complete separation, such as in removing benzole from coke-oven gas by refrigeration with liquid ammonia and in the separation of helium from natural gas by liquefying all the components except helium. But in most cases liquefaction leads only to a partial separation of the mixture.

Partial liquefaction yields liquid and gaseous phases in thermodynamic equilibrium with one another. Such a system has the same temperature and pressure throughout, but different concentrations in the two phases. Its practical significance lies in the formation of a definite and permanent phase boundary across which a finite concentration head is set up and maintained indefinitely. Generally one such phase boundary is insufficient and there must be several boundaries each with its own concentration head. A device which enables a series of phase boundaries to be maintained, across each of which the composition of the mixture changes by a finite amount, is a fractionating column, more especially a plate column with its finite number of rectifying plates each leading to a definite change in the composition of the mixture passing through it. A packed column may be considered as containing an infinite number of plates, each providing an infinitely small change in composition. The significance of the plate column lies in the fact that the concentration heads are maintained in accordance with the laws of phase equilibrium. The physical phase boundary is that between the liquid on the plate and the bubbles of gas passing through it. The metal plate is merely a frame allowing the physical phase boundary to be set up and maintained. For all finer processes of gas separation, *i.e.*, when components are to be separated whose thermal properties are not too far apart, a fractionating column is an essential part of the equipment.

It is thus evident that the principal tools of gas separation are: (1) refrigerating plant, such as compressors, condensers, evaporators, expansion engines, and turbines, and (2) fractionating plant, such as columns and dephlegmators. To these must be added (3) machinery for the exchange of heat, *i.e.*, heat interchangers and cold accumulators, and finally (4) in most cases some preliminary absorption device for removing impurities such as water and CO_2, which must be removed because they solidify at relatively high temperatures. Lagging plays an important part in the efficiency of all gas-separating plants, more especially in the smaller units, and this should properly be included in the items of refrigerating equipment.

Problems and their Solution.

(1) *Air separation in the double column.*—It is well known that the production of oxygen and nitrogen from atmospheric air is normally carried out in two fractionating columns, one placed on the top of the other, the lower column working at a pressure of 4–5 atm. abs. and the upper column working at atmospheric pressure. It is of interest to ascertain why this arrangement was found necessary and why it has been maintained in industrial practice without notable changes for 35 years.

In the rectification of spirit and in the separation of most binary systems above room temperature, a single column has been found sufficient. The liquid mixture is introduced in the middle, is partially rectified in the exhauster, evaporated in the sump, and finally rectified in the concentrating column above with the help of the reflux from the condenser. Why is this simple device inadequate in the case of air?

The reason is to be found in the particular circumstances of the low temperatures involved and the consequent refrigerating requirements. In separation above room temperature, where no refrigerating machinery is needed, there is no necessary relation between the heat supplied to the boiler and that withdrawn in the condenser. Steam and cooling water are generally available in any required quantities and are quite independent of one another. In the separation of air at low temperatures, where no

FIG. 3.

DEVELOPMENT OF DOUBLE COLUMN.

foreign refrigerants are available, the cold must be supplied by the air itself. The only way in which heat can be withdrawn from the condenser is by evaporating liquid air or one of its constituents. The only cold liquid available is that formed in the evaporator, and this, in the case of a single column, is pure oxygen. But the liquid reflux from the condenser must be colder than the liquid in the evaporator, and so the refrigerant in the condenser must be colder still—colder than pure liquid nitrogen and much colder than liquid oxygen, whose boiling point is 13° C. above that of nitrogen. Since it is impracticable to work at pressures far below atmospheric, the only way out of the difficulty is to raise the pressure in the column to such an extent that the boiling point of nitrogen at this pressure becomes higher than that of oxygen at 1 atmosphere. It is then possible to take liquid oxygen from the evaporator, expand it to atmospheric pressure, thereby lowering its temperature, and to use the latent heat of vaporization of this oxygen to condense nitrogen at the elevated

pressure, thus obtaining the necessary reflux. This explains why the separation of air has to take place partially at a pressure of about 4 atm.

This is only one step, however, towards solving the problem. Air contains about 79% nitrogen and 21% oxygen, neglecting the argon at this stage of the argument. If pure liquid oxygen were collected in the evaporator, that liquid would be insufficient to produce the necessary reflux in the condenser. There would not be enough refrigerant available. To overcome this difficulty, the liquid oxygen in the evaporator has to be heavily diluted with nitrogen. It can be shown theoretically that the

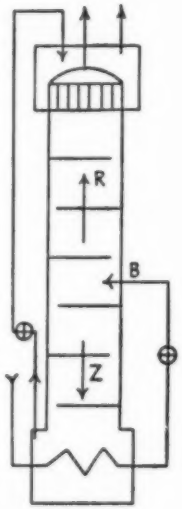


FIG. 4.
DEVELOPMENT OF DOUBLE COLUMN. SECOND STEP.

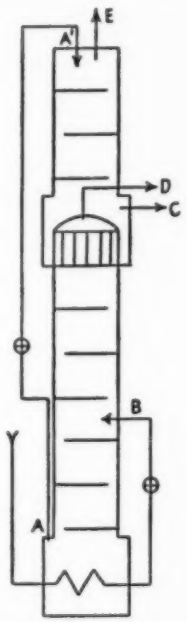


FIG. 5.
DEVELOPMENT OF DOUBLE COLUMN. THIRD STEP.

highest oxygen concentration permissible in the sump is 60%. In practice the liquid contains about 45% oxygen. This secures the correct balance in the condenser for producing the reflux and enables pure nitrogen to be obtained at the top of the column. There is then the problem of purifying the 45% oxygen mixture. This is achieved by taking another step forward in the direction of the double column : a number of plates are inserted between the inlet of the expanded liquid oxygen and the condenser. However, though this procedure can and does lead to pure oxygen in the intratubular space of the condenser, the vapour passing upwards from the oxygen inlet cannot contain more nitrogen than is in equilibrium with the liquid oxygen entering the upper column. This vapour will contain about

15% oxygen, which will be lost unless the rectification is continued above the inlet. To produce a reflux in the upper part of the low-pressure column, a refrigerant is available in the form of the liquid nitrogen formed in the condenser. The final step is achieved, therefore, by withdrawing some liquid nitrogen from a trough below the condenser, expanding it to atmospheric pressure, and introducing it at the top of the upper column,

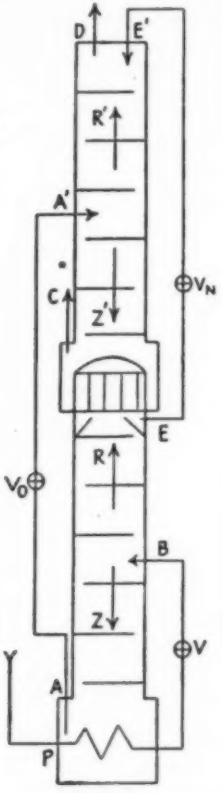


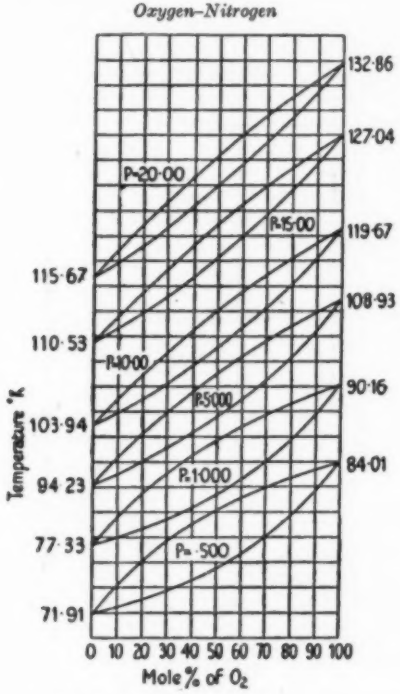
FIG. 6.

LINDE DOUBLE AIR COLUMN.

where it completes the rectification by replacing the oxygen in the vapour rising from the liquid inlet.

It will be seen from this analysis that the double air column is not just one of many possible chance solutions which has been retained in the industry by conservatism or lack of enterprise, but a logical development of applying the well-known principles of rectification to a mixture of gases with very low boiling points, where the only refrigerants available are the mixture treated and its liquefied components.

The double air column, as originally patented by Linde in 1908 and subsequently used, with certain unessential modifications, in most industrial plant, enables pure oxygen and pure nitrogen to be produced simultaneously. In practice this is not usually attempted. Most industrial plants are designed either for pure oxygen (99·6 per cent.) or pure nitrogen, the other component being somewhat impure. The large Linde plant for delivering nitrogen for the ammonia synthesis yields 99·5 per cent. nitrogen



(T, x) CURVES AT 0·5, 1, 5, 10, 15, AND 20 ATM. DODGE AND DUNBAR, "CIRCULATION METHOD."

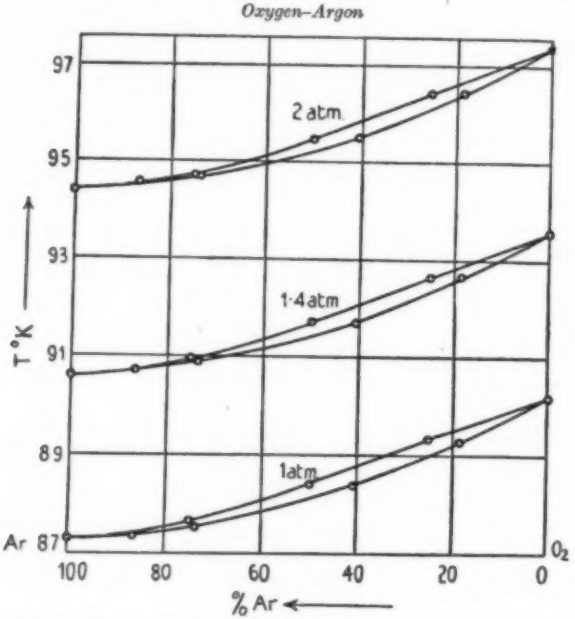
and 94 per cent. oxygen. Some German and Russian plant can be adjusted to yield either component pure, as desired.

One of the reasons why the simultaneous production of pure oxygen and pure nitrogen is not practicable is that it would require more plates than are economically justified. The other reason is more profound and is worth more detailed consideration.

(2) *The Separation of Argon from Air.*—Atmospheric air contains 0·94 per cent. argon. Though the concentration is low, the presence of argon is important for two reasons. Firstly, argon is a valuable element, especially for filling incandescent bulbs. Secondly, the presence of argon

makes it virtually impossible to obtain pure oxygen and pure nitrogen at the same time.

The boiling point of argon lies between the boiling points of oxygen and nitrogen, and is only 3° C. below that of oxygen. During the rectification of air in the double column, argon accumulates, more especially in the lower part of the upper column, where its concentration can be 12 per cent. or even higher. As a result, it is possible to withdraw an "argon fraction" from this part of the double column, containing between 7 and 10 per cent. of argon, which can then be further rectified to give technical argon for filling lamps. It is much more economical to obtain argon from a



(*T*, *x*) CURVES AT 1, 1·4, AND 2 ATM. BOURBO AND ISCHKIN. "BOILING-POINT METHOD."

FIG. 7.

10 per cent. concentrate than from a mixture containing only 1 per cent. On the other hand, if the argon fraction is not withdrawn, the lower part of the upper air column is wholly concerned with separating the argon from the oxygen. The nitrogen content of this part of the column is negligible.

It is very much more difficult to separate argon and oxygen than nitrogen and oxygen, owing to the proximity of the boiling points. A correct estimation of the function of such a column, more especially of the number of plates required, is impossible without a knowledge of the liquid-vapour equilibrium of oxygen–argon mixtures, just as the design of

air-separating plant presupposes a knowledge of the oxygen–nitrogen equilibrium, which was furnished by the classical papers of Baly [1] and of Dodge and Dunbar.[2] A study of these mixtures was undertaken by Bourbo and Ischkin,[3] in the research laboratory of the Russian State organization known as VAT., which is principally concerned with building air separating plant. The results are shown side by side with those for oxygen and nitrogen, where the curves for dew-point and boiling point are very much farther apart. Clearly the separation of oxygen and argon requires more plates than that of oxygen and nitrogen.

The theory of argon concentration in an air column was developed by Hausen [4] of the German Linde Company on the basis of a theoretical diagram for the liquid-vapour equilibrium of the ternary system. The result of this work has been to show that, in all large-scale plant, it is advisable to combine oxygen and argon production. Not only does the removal of the argon fraction from the correct point in the lower column allow the production of technical argon in one auxiliary argon column, but the withdrawal of this fraction materially assists in obtaining pure oxygen in the primary air column.

(3) *Problems of Coke-oven Gas Separation.*—The Linde–Bronn process for the separation of coke-oven gas is one of the most highly developed and complicated processes of gas separation, the object being to obtain a 3 : 1 mixture of hydrogen and nitrogen for ammonia synthesis. It is in some ways superior to the Claude process in that it yields purer products. Initiated in Germany shortly after the last war, it was introduced into the Soviet Union in 1932, where it has since been considerably developed and diligently studied, especially at the Low Temperature Research Station at Kharkov, where most of the scientific data required for calculations have been obtained during the five years before the German invasion.

The process consists in cooling the coke-oven gas, compressed to about 12 atm., to a very low temperature, condensing out a series of fractions and leaving finally hydrogen and nitrogen as the product. The refrigerant is liquid nitrogen obtained from a separate air-separating unit. Apart from its rôle as a refrigerant, the nitrogen has two other tasks to perform; it is used to scrub carbon monoxide out of the product, the presence of which poisons the ammonia catalyst, and it is added in sufficient quantities to bring the product to the correct concentration.

Apart from the usual questions of heat-transfer coefficients, viscosities, and latent and specific heats of cold liquids and their mixtures, the design of large-scale plant of this nature presents a number of problems owing to the complex composition of coke-oven gas. As shown in Table I, coke-oven gas includes six components in concentrations over 1 per cent. and numerous impurities in smaller concentration whose presence interferes with the separation process. In addition to moisture and carbon dioxide, there are a benzole fraction containing benzene, toluene, and some metaxylene, which is only partly removed at source, a certain amount of naphthalene and traces of sulphur compounds.

The main fractions of coke-oven gas are the ethylene, methane, and carbon monoxide fractions, each of which contains two or more components. It is essential to know the compositions of these fractions, as

they depend on temperature, pressure, and the composition of the original mixture. This involves a detailed study of liquid-vapour equilibrium of binary and ternary mixtures at various pressure and temperatures. Some of these mixtures have been studied in England, notably by Verschoyle[5] and, more recently, by a group of scientists in the Imperial College.[6] However, most of the work was done at the Kharkov Research Station and in some other Russian laboratories.[7] There are now available all the requisite data on the liquid vapour equilibria of ethylene and ethane, ethylene and methane, ethane and methane, and their ternary mixture,

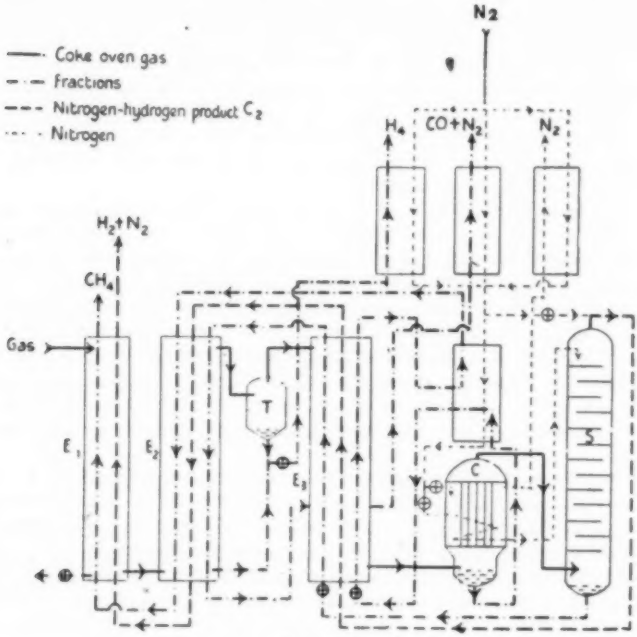


FIG. 8.

THE LINDE-BRONN PROCESS FOR SEPARATING COKE-OVEN GAS.

covering the requirements of the ethylene fraction. There is also all the information required on the following mixtures which occur in the methane fraction: methane–nitrogen, methane–hydrogen, hydrogen-methane–nitrogen, and, finally, for the carbon-monoxide fraction, hydrogen-nitrogen, hydrogen–carbon monoxide, and hydrogen–nitrogen–carbon monoxide. A detailed study has been made of the scrubbing column and the process of replacing carbon monoxide with nitrogen by scrubbing the mixture with liquid nitrogen,[8] and a new thermodynamic diagram of nitrogen has been constructed,[9] replacing the faulty Dutch diagram and extending to higher pressures the diagram issued by the American Bureau of Mines. Finally the Kharkov scientists have determined the viscosity

in the liquid phase of all the components of coke-oven gas at all temperatures between the triple points and the critical points and have investigated a large number of binary mixtures.[10]

Experiments on semi-scale plant, also made at Kharkov [11] have established the possibility of obtaining technical hydrogen from coke-oven gas on a commercial scale with a purity of over 96 per cent., and work has been commenced with a view to obtaining pure ethylene from the same source for chemical synthesis, more especially for the synthetic rubber industry.[12]

The benzole fraction in coke-oven gas has long been a source of trouble to chemical engineers. Its removal by absorption is expensive and not

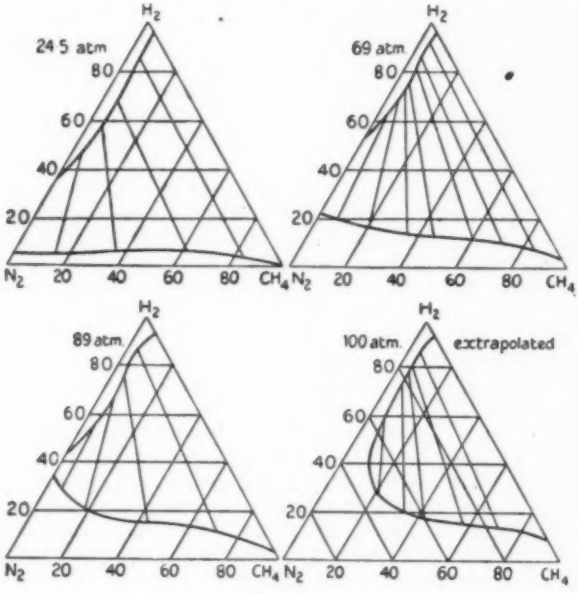


FIG. 9.

METHANE–NITROGEN–HYDROGEN.

always efficient and attempts to dispose of it by condensation at low temperatures have frequently led to solidification and consequent blockages of pipes. In order to remove the last traces of benzole vapours, it is necessary to cool the mixture to about — 45° C. with liquid ammonia, and to do this successfully we must know what concentrations of benzene, toluene, and xylene are still liquid at these temperatures. This problem was attacked with considerable success by B. M. Kravchenko [13] at Kharkov, who determined the solidification curves of the ternary mixtures benzene–toluene–metaxylene and benzene–metaxylene–naphthalene and constructed a solid model showing the course of the eutectic curves. He has since devoted himself to the still more complex and arduous problem

of the quaternary mixtures, and the first results were published in the last Russian journal to reach these shores.

It can now be said that the scientific data required for the full development of coke-oven gas separation are available. The path is free for an extension of the process to the production of other fractions and components apart from a mixture of hydrogen and nitrogen and for the separation of other gases of somewhat different composition but containing essentially the same components in different proportions. Also, from a scientific point of view, valuable data have been obtained for the elaboration of a theory of the liquid state and for the thermodynamics of mixtures and solutions.

In this paper it has not been possible to touch on all the existing processes and problems of gas separation, each of which possesses its own points of interest. Thus, the production of olefines from cracker gases and the separation of helium from natural gas have given rise to important scientific and technical developments. It is hoped, however, that the general character of the problems involved has been indicated by the examples chosen.

The industry of gas separation is still young and it has a great future before it. Even in the complicated world situation of to-day the trend of its development can be foreseen. It will be towards larger units and a greater use of cold liquids. The pressing problems of fuel economy and the need for the raw materials for chemical synthesis on a large scale will force this issue, so that it will no longer be permissible to burn away any gas mixture that happens to be available without regard for the relative value of its components. The advantages in the storage and transport of liquids over that of gases will drive us to learn how to handle cold liquids in large quantities.

The consequence of the increase in the size of plant and the removal of cold liquids will raise as the main issue in gas separation that of economy in power, a point which has hitherto been somewhat neglected. As long as the plant is small and the products are withdrawn at room temperature, power is only a small factor in production costs. With large plant, which cheapens the labour factor, and the added cost of refrigeration for yielding cold liquids, power becomes the predominant factor. This will lead to new methods in refrigeration, of which a further development of the absorption method and the general use of mixed refrigerants will in all probability be a prominent feature.

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DISCUSSION.

A JOINT Meeting of the Institution of Chemical Engineers, the Institute of Petroleum, and the Chemical Engineering Group (Society of Chemical Industry) was held at the Institution of Mechanical Engineers, London, on Tuesday 14th July. Mr. C. S. Garland (President, Institution of Chemical Engineers) was in the Chair, and a paper on "The Separation of Gases" was presented by Dr. Martin Ruhemann. (See page 215.)

DR. P. M. SCHUFTAN raised one or two points of a practical nature. He suggested that it was perhaps not quite true when the author said that the cascade process was not employed to any great extent industrially. The Americans used it for air separation, and in some form or another it was being used quite a lot for the separation of complicated hydrocarbon mixtures.

The author had rightly stressed the importance of producing cold at the lowest possible cost and referred to the use of expansion engines. It was perhaps not generally known that the expansion engine, especially of the Heylandt type, was very efficient and even expansion turbines, which had been used in the past and were now being proposed again, would hardly be able to compete.

There was a very large field to work in connection with coke oven gas separation, but it should be realized that a great deal had been done apart from the Russian plant mentioned, although that was one of the largest plants in the world. There were scores of coke-oven gas separation plants all over the world, mostly producing the hydrogen–nitrogen mixture required for ammonia synthesis, but also some producing hydrogen up to 98 per cent. as required for hydrogenation, while others were producing by-products such as methane and ethylene.

MR. PHILIP BORCHARDT said this paper gave him an opportunity of making some remarks about gas separation, partly of historical and partly of technical interest.

The development of the double-column air separator had a predecessor in Mr. G. Claude's "liquefaction sous pression avec retour en arrière." The column of Mr. Claude was therefore the first to adopt rectification of air in two steps, then a great achievement fully appreciated by the late Prof. von Linde. It was, however, possible to produce "pure" nitrogen before Mr. Claude introduced double rectification and, in fact, Linde had supplied as early as 1904 several plants producing nitrogen with about 0·1 per cent. oxygen using a nitrogen circuit and a single-column rectification. The double rectification, however, gave the great advantage of dispensing with this circuit. Linde considered the Claude principle of using a reflux condenser as first step in rectification was not entirely satisfactory, and he replaced this condenser by a normal rectification column working, as Dr. Ruhemann had pointed out, at 4 to 5 atmospheres, and he remembered the first separator unit of this kind he had the honour to construct in 1910. Yield and purity of the products of these separators were, of course, not satisfactory, compared with the results of a modern separator.

A single rectification column gives theoretically, when producing pure oxygen, a waste nitrogen of about 7·5 per cent. oxygen content—practically 8–9 per cent. The first double-column separators brought this figure down to about 3 per cent. Since then the improvement, due mainly to the increasingly better effects of the rectification trays of modern design, had resulted in the following state of air separation: When liquid oxygen is the product to be obtained, the yield of a modern Heylandt plant, using Linde rectification columns, was nearly 20 per cent. of the air to be separated. In the case of gaseous oxygen and/or nitrogen to be produced, the

air might be separated in oxygen of 99–99·5 per cent., and in absolutely pure nitrogen produced simultaneously a small portion of not more than 8 per cent. of the air to be withdrawn from an suitable point of the upper column in the form of a waste oxygen with 40–50 per cent. oxygen content. This withdrawing of a small amount from somewhere between the top and the bottom of the upper column was necessary not only, as mentioned by the author, for the elimination of the argon, which otherwise would be trapped in the lower part of the column, but also to stabilize the operation of the separator, because any change of the working conditions inside the unit would result in an impurity of one of the products, if not, the third or waste fraction would be withdrawn.

The reason why some of the Linde plants for the production of pure nitrogen were not designed for a simultaneous production of pure oxygen, but only for about 93 per cent. of waste oxygen, was the fact that the nitrogen to be used for ammonia synthesis had to be as far as possible free of argon, and the simplest way to obtain that was to produce the oxygen with not more than about 93 per cent. The simultaneous production of both oxygen and nitrogen of highest purity had been adopted everywhere where the buyer of the plant was interested in both products.

With regard to the purity of the products obtained by a modern Linde plant, nitrogen with no more than 20 parts per million of oxygen was nowadays a standard product, such nitrogen no longer giving any mists when brought in contact with phosphorus. Further, the argon content of such nitrogen, as proved by the operation of modern ammonia synthesis, was negligible.

The power consumption of a modern air separator was mainly dependent on the size and purpose of the plant. All bigger plants were still based on the use of the Joule–Thomson expansion using, however, high- and low-pressure air. It was remarkable what an enormous influence the very simple experiments carried out by Joule and Lord Kelvin had on modern life through the application of their results on gas separation by the late Professor Linde. Not enough emphasis could be laid on the fact that the whole of the work done on gas separation with most of the applications was originated in this country through the work of British scientists, whilst the technical and industrial application of this work was carried out by scientists in other countries.

Mr. George Claude, the eminent French scientist, had achieved many improvements in gas separation, and it would be unfair not to mention his merits. The introduction of liquefaction under pressure had already been mentioned. His other inventions were characterized by the use of an expansion engine for a part of the air instead of the Joule–Thomson throttle valve, and later he developed the production of rare gases in pure form from air. In this same connection should be mentioned the work of British scientists such as Sir William Ramsay and Travers which had been of enormous technical value.

With reference to the Claude liquefaction principle, it was remarkable that Linde had applied the same process during the last decade before the war in smaller units for oxygen production, the expansion engine giving special advantages in simplicity, and lower power consumption than the Joule–Thomson expansion, if the units are so small that the Linde process for high and low pressure could not yet have been usefully applied. Bigger units were now mostly applying this principle of high and low pressure and gave even lower power consumption than the Claude process, with many other advantages. The biggest units of this kind were for about 9000 cu. metres of air giving 6800 cu. metres of pure nitrogen and 1600 cu. metres of pure oxygen per hour. The argon production was not a very important matter, nor were neon and helium, for they were in the air in such minute quantities that their production was a speciality of only a few makers.

As the author had said, krypton was an interesting gas, but there were many conflicting opinions about it, and he warned people against putting too much hope on this gas. Linde had constructed a big krypton plant in Hungary, where the krypton was promoted violently. Some 50,000 cu. metres per hour of air were separated in this plant but, of course, not liquefied entirely, because the boiling point of krypton was so high that it could be separated from the bulk of the air in a kind of reflux condenser. There was still a certain difficulty to be faced in condensing only the highest boiling constituents of the very large quantities of air because of the very small content of acetylene which was present in the air everywhere, and which accumulated in the condensate together with the krypton. Special precautions had

to be taken to cope with this danger, which in the past had done so much harm to the separation of air, but in all normal plants this problem had been solved satisfactorily nowadays.

With regard to coke-gas separation, it was of importance that this process became of interest when and where there was an excess of coke gas available without any possibility of using it.

The extraction of hydrogen from gas mixtures like water gas was an old and well-known process. For instance, there was in this country at Selby before the first world war such a plant under construction. It was Bronn who pointed out that the combination of gas-coke separation and ammonia synthesis would be an interesting process. The Bronn patent was famous in the twenties and thirties of the present century, although it gave but little advice as to how the coke-gas separation could be carried out. Moreover, so little was known apparently about the most valuable and important invention of Mr. Maxted, now used in every coke gas separation for ammonia synthesis, that Dr. Ruhemann did not even mention Dr. Maxted in his book "Gas Separation." The Maxted invention dealt with the scrubbing of gas mixtures like coke gas by liquid nitrogen in order to remove the CO content and replace it by nitrogen. Linde obtained the licence for the use of this invention, without the use of which it would not be possible to produce the CO free hydrogen–nitrogen mixture now produced all over the world in numerous partly very important works. The importance of the Maxted process was made clear when it was pointed out that this purely mechanical procedure in the form Linde had given to the process resulted in at least the same purity of CO as the best chemical absorption methods—for instance, scrubbing with cupreous ammonia formiate. It was possible nowadays, however, by using the Linde–Maxted process to dispose of a pre-catalyst in the ammonia synthesis, which catalyst had been necessary in the earlier years when the process had been developed in order to remove the last traces of CO. Without the great success of the Linde coke-gas separation process it would scarcely have been possible that the other constituents of the coke gas could have found so much interest as had been the case in recent years.

Ethylene produced in the normal Linde plant as a fraction already rich in olefines can be purified to any wanted purity. Methane is a by-product which so far had been neglected by the chemical industry, but the electric-arc process developed in the U.S.A., for transforming methane into a mixture rich in acetylene, had changed the situation, and this process was now used in a Buna plant for the production of artificial rubber where the by-product methane of another important Linde coke-gas separation was available. Therefore, many modern Linde coke-gas separation plants were now producing, besides the hydrogen–nitrogen mixture or pure hydrogen, pure ethylene and pure methane, whilst the coke-ovens were burning cheap producer gas instead of the valuable coke-gas or the constituents thereof. All this progress was partly due to the Maxted invention and partly, of course, to other contributions of Linde and their engineers.

It would also be unfair not to mention that a great part of this work had been done by Dr. Schuftan, now also in this country. The analytical work, the investigation of the equilibria of the coke-gas constituents, the research work connected with the many tricky matters in the operation, and many other scientific and practical achievements in this field stood to his credit, and this work had been carried out long before the Russian engineers commenced their research work.

The author mentioned the production of nearly pure hydrogen from coke gas. The actual purity of such hydrogen in a modern Linde plant was 98–99 per cent., the purity depending mostly on the size of the vacuum pump for nitrogen by which the lowest temperatures in the process were obtained. As these temperatures were below the dew-point of air, special care had to be taken in the design of those parts of the unit subject to these temperatures, in order to avoid the air condensations on the surfaces of the cold parts. The latest model of hydrogen units of this kind operated in a plant for hydrogenation purposes, including the production of pure ethylene, was separating 12,000 cu. metres of coke gas per hour.

Although very large quantities of ethylene were produced by all these plants, it seemed that the hunger for still more ethylene had to be satisfied. As early as 1936 he himself had suggested the possibility of producing ethylene from coke gas by using the regenerator principle which so far had been applied only on the Linde–Fraenkl plants for air separation. Such a plant had been constructed by Linde in

1938 as a pioneer plant, the idea being that no other constituents of the coke gas besides ethylene should be recovered.

Summing up, Mr. Borchardt expressed the hope that after the war a powerful and independent industry would be developed in this country for gas separation, which would supply plants of any description and for any gas, for instance, oxygen or nitrogen, hydrogen or ethylene, to everyone who had so far been depending on foreign makers. The paper demonstrated that there were experts in this country available for this.

Mr. T. P. Dee said this paper was of particular interest to his Company, as they were operating both a Linde double-air column and a Lindre–Bonn plant for the separation of hydrogen from coke-oven gas, the hydrogen being used for the synthesis of ammonia. They intended to study the recent work in Russia to which the author had referred. He gathered from the paper that the production of argon in an auxiliary column assisted in obtaining both nitrogen and oxygen in a high degree of purity from the double air column. It would be interesting, however, if the author could say what future there was for argon, in view of his statement that a krypton–xenon mixture was much better for incandescent bulbs.

Mention was made in the paper of three purposes for which nitrogen was used in separating coke-oven gas—viz., for scrubbing out carbon monoxide, for refrigeration, and to mix with the hydrogen to give a 3 : 1 mixture. In their plant they used normally 14 cu. ft. of nitrogen per 100 cu. ft. of hydrogen for scrubbing purposes, and 9 cu. ft. for evaporation in the nitrogen vessel, where it brought about the final cooling of the gas. It would interest him to know how these figures compared with modern practice in Russia. Could the author also say what was the pressure at which the nitrogen was usually maintained in the evaporator in Russian practice?

Mr. R. J. Low said that when, some years ago, he investigated the question of hydrogen production, several points came out. A great deal was heard about the power required, but nobody had mentioned how little power was theoretically required. He believed that one American inventor had claimed to get down to 3 kw. per 1000 cu. ft. of oxygen, and it would be interesting to know how much power was required, first, if an infinite number of heat exchangers were used on a theoretic basis, and secondly, if a definite number of heat exchangers were used—say one, two, three, or four. It was rather like stage feed-heating with turbine plants.

The question of working up the gases was a very interesting one, and a really definite effort had been made to extract everything possible out of coke-oven gas before using the hydrogen. A great point had been made of collecting ethylene and working it up into products worth about £110 per ton instead of merely burning it under the coke-ovens.

On the question of power, he said that on the average plant the power was comparatively easily obtained, but many chemical works did not consider degrading their heat stage by stage. The first portion could go under the boiler-producing steam, then taking the steam to the turbine or engine, and then using the waste heat from the engine in an evaporator, perhaps for the boiler plant, or in some other way. The same might apply to the flue gases, and it would be interesting to hear what could be done in that way on plant for the production of oxygen partly worked by steam to produce power and partly by the waste heat from the steam to produce the refrigeration effect. Where oxygen was produced for the purpose of making nitrogen, if steam plant was used the possibilities might be considered of putting oxygen into the combustion air for the boilers. If anybody was afraid of burning the boiler out, consideration might be given to the fact that it was always possible to use the re-circulation of gases to get mass flow and maintain the heat transfer without getting over-temperature in the furnace.

With regard to large plants, no mention had been made of a point which was brought out a few weeks back in *The Engineer* or *Engineering*. In America large quantities of natural gas were liquefied with a view to storage. Large quantities of natural gas were available, but the demand fluctuated due to climatic conditions in the city where it was used. Those concerned went into the question of pipe-lines

and also using ordinary atmospheric pressure hydration, but they found the best way in the end was to use three-stage refrigeration and actually liquefy the whole of the peak load of the gas and keep it stored in liquid form until it was required—say, when there was a cold snap. There seemed to be a very great future for that.

As to the Selby plant that had been mentioned, he remembered finding out about that in the Patent Office, but he would like to know more about it. Hydrogen on a small scale seemed to have been produced economically. It started off with water gas to get hydrogen, and used the CO in particular to run a gas engine to produce the power. In this connection he thought the old-fashioned gas engine might be considered when using coke-oven gas.

With regard to hydrogen production, some time back he investigated the possibilities of producing hydrogen directly from coke in an electrolytic plant, and also of taking cheap coke breeze and using that in a gas engine to produce the power for electrolytic production. One interesting thing arising from this was that, rather to his surprise, the gas engine was roughly as efficient as steam plant. He did not go into the question of the gas engine from the point of view of producers. If one wanted to work up the mixed gases, one way would be to take the gases, separate them, use the hydrogen for the purpose for which it was required, and use the waste gases to drive a gas engine, and use the waste heat from the gas engine, which was usually 30 per cent. of the original heat, in the form of power, and have a waste-heat boiler for working an absorption machine for producing cold. Speaking of the absorption machine, he said that some time ago the problem arose of getting a temperature between what was usually associated with an ammonia machine and liquid air, and he was assured by a manufacturer that the absorption machine could easily get down to $-100°$ C.

Mr. J. A. Oriel remarking that, although the meeting had been arranged as a joint conference, he felt that the petroleum industry seemed to have had a rather poor show so far. He felt scarcely qualified to speak on the subject or the technical aspects of the separation of petroleum gases. He might say something which would inspire those present who did know a good deal about them to give some technical data. To get a sense of proportion in this matter he directed the attention of the meeting to the fact that a considerable amount of work in gas separation had been carried out in the petroleum industry during the past 15 or 20 years. The author had given analyses of cracked gas and natural gas, and these gases had been the foundation of what might be called a complete new industry in the United States—*i.e.*, the industry of chemicals and solvents built up entirely on cracked and natural gases. This had only been made possible by the work carried out on the separation of gases in order to obtain them in the pure state. It was true he was not speaking of the same order of refrigeration as had up to then been considered during the discussion; nevertheless, the order of purity with which these gases had been obtained had enabled a whole new industry to grow up; which industry was responsible for a considerable number of materials necessary for the Allied Nations. The industry which most readily leapt to mind was the synthetic rubber industry, which was now growing to very large proportions in the United States based on the separation of gases from the cracked gas industry. There was also the production of acetone, glycerine, and several other pure chemicals that could only be obtained in their pure state due to the very fine fractionation that had been developed for gases in the petroleum industry.

Mr. R. P. Donnelly said that a few years ago he was seeking information on the separation of oxygen, and it was difficult to find any references. The only one he could find was one in the *Journal of the American Chemical Society* in 1928 in connection with some work by Dodge. What was definitely needed in industry, and particularly those industries which would be using oxygen in the post-war period, was precise figures of power costs as compared with the size of the plants and oxygen producing units. The nearest figure he could get was for the Linde process, and it was 20 h.p.-hours per 1000 cu. ft. of oxygen. With the Linde–Fraenkl process using the regenerative system instead of the recuperative system the figure was about 15 h.p.-hours per 1000 cu. ft. of oxygen, the lower figure being for a more impure oxygen. Did that represent the limit, or how much could it be improved by increasing the

size of the plant? It was on such matters as these that the non-specialist at present was at a loss.

THE AUTHOR, replying to the discussion, said that he could not answer all the questions that had been put, even if he were in a position to do so, in the short time available, but that he would like to make a few comments. All the contributions had been extremely helpful, and had supplemented what he himself had said.

He would have liked to deal more fully with the separation of coke-oven gas, especially with the methods of obtaining other products besides a nitrogen–hydrogen mixture, such as pure hydrogen, methane and ethylene, and he was glad that these points had featured in the discussion. He regretted not having mentioned Dr. Maxted as the inventor of the process for scrubbing out carbon monoxide with liquid nitrogen.

In reply to Mr. Dee's question as to the nitrogen pressure used in Russian plant for separating coke-oven gas, he believed that the nitrogen was compressed to 180 atm. and evaporated in the methane condenser at just over 1 atm. pressure when a nitrogen–hydrogen mixture was to be produced. However, much lower pressures were necessary when the product was to be almost pure hydrogen. To obtain 96 per cent. hydrogen, about 0·35 atm. were needed and, to judge from Mr. Borchardt's remark, he supposed that about 0·2 atm. were used in Germany, as otherwise he did not think it would be possible to obtain hydrogen of a purity of 98 or 99 per cent. In the Russian plant for producing the mixture for ammonia synthesis about 170 cu. ft. of nitrogen were used for 1000 cu. ft. of coke-oven gas.

It was clear that, as Dr. Schuftan and Mr. Borchardt had said, much valuable research work had been done on the components of coke-oven gas and their mixtures before the investigations made in Russia. Without this it would have been impossible for the Linde Company to design their plant. However, not very much of this work was available in the literature.

He was very glad that reference had been made in the discussion to gas separation in the petroleum industry, because he felt that insufficient consideration had been given to the very valuable work done in America on the separation of light paraffins, especially the investigations of Kay, Sage, and Lacey on the liquid–vapour equilibrium of mixtures of methane, propane, butane, etc.

With regard to power consumption in the production of gaseous oxygen, the figures given by Mr. Donelly were, in the main, correct, and he himself could give some figures which also indicated the influence of the size of the plant. In the following figures the size of the plant was given in cu. metres of oxygen produced per hour and the power consumption in kw.-hours per 1000 cu. ft. of oxygen.

Power Consumption in Oxygen Production.

Cu. m./hr.	Kw.-hr./1000 cu. ft.
10	48
30	29
80	23
200	21
500	19
8000	12·7

The last figure referred to 98 per cent. oxygen and corresponded to the 15 h.p.-hours mentioned by Mr. Donelly. Personally he did not think it was possible, with present technique, to get very much lower than this figure, because the Linde–Fraenkl system was extremely efficient.

He agreed with Mr. Low that absorption refrigeration had a very great part to play in the future. He believed that it would be quite possible to achieve a temperature of — 100° C. with the extensive use of absorption methods. In this connection he would direct attention to the work of Dr. Altenkirch in Germany on reversibly absorption machines and to the work carried out in this country by the late Dr. Maiuri on obtaining low temperatures with absorption methods. It was particularly

important that the absorption machine enabled the extensive use of waste steam, which would be a great step in the direction of power and fuel economy.

He also had been greatly interested in the work quoted by Mr. Low on the storage of liquefied natural gas in America, as showing the possibilities of large-scale gas liquefaction. He regretted that the authors of this paper had made little mention of the difficulties which must have been encountered.

In a written reply to Mr. Dee's question regarding the future of argon, the author expressed the opinion that this could not be foreseen, just as it was impossible to foresee the future of incandescent bulb lighting. He thought it probable that incandescent bulb lighting would be largely replaced by discharge lighting before the argon–krypton question had been answered, and thereupon the same problem would reappear on a new level. The importance of argon lay in the fact that it was a necessary by-product, which krypton was not, and that there was 10,000 times more argon in that air than krypton.

Finally the author agreed with Mr. Bagley's written suggestion that the subject here dealt with should take its place in the University. If, as Mr. Borchardt hoped, a powerful and independent gas-separating industry was to be developed in this country, research on a scale compatible with that carried on in the U.S.A. and the U.S.S.R. was a necessity, and facilities for such research would have to be provided.

Mr. S. J. Tungay (Chairman, Chemical Engineering Group), proposing a vote of thanks to the author said they had listened to a fascinating paper which reminded them of how Nature, that great and incomprehensible alchemist, appeared easily to separate gases and apply the various fractions for her own purposes and then showed how difficult it was when science and industry endeavoured to accomplish the same thing and apply the fractions to industrial purposes. The study was a fascinating one but, as the author had said, the industry was still a young one, and a deep debt of gratitude was owing to him for bringing this subject forward so effectively. The author had so simplified details of this complicated and complex system that " he who runs may read," and they had had a most enjoyable evening.

Mr. Ashley Carter (Institute of Petroleum) seconded the proposal and included in the vote of thanks those who had taken part in the discussion. He expressed regret that so few members of the Institute of Petroleum were present, but on behalf of the President and members of the Institute he expressed appreciation of the opportunity afforded by the Institution of Chemical Engineers and the Chemical Engineering Group to attend this joint meeting. He imagined that the paper and discussion would be published in the Institute's *Journal* so that all the members would have an opportunity of reading what had taken place and what had made the evening such an interesting one.

The vote of thanks was cordially given.

Mr. D. Bagley writes : the three Institutes who have sponsored this contribution to science are to be congratulated. Dr. Ruhemann's paper is of value to industry, as he is one of a very limited number conversant with large-scale research and practice in the development of gas separation.

As Dr. Linde's Chief Engineer was present at the meeting, I may recall that the late Mr. Murray, Chairman of the British Oxygen Company for many years, introduced my firm to Linde's at a time both were pursuing the oxygenated blast, which terminated with practical application at Gutehoffnungshutte, and not, as we originally determined, in Cumberland. The Iron and Steel Federation thoroughly investigated this development following the computations of the late Mr. Saniter and myself, and rightly concluded that the returns were inadequate, although I believe they were in agreement as to the economy to be secured in reducing the coke consumption with a furnace running on ferro-manganese.

Of particular interest to-day is the separation and liquefaction of the methane fraction in coke-oven gas, as also the liquefaction of marsh gas ex the Collieries, and sewage gas. Dr. Borchardt informed me before I entered the hall that not much further progress had been made in Germany. I may cite *Automobiltechnische Zeitschrift* (10th Sept., 1938), which indicates six gases suitable for motor use, and in particular " Motoren Methan," probably consisting of 70 per cent. CH_4, with varying

percentages of propane and butane, an interim stage between the compressed gas and the liquefied gases. The number of cars propelled by these gases in Germany is well known. If we consider the low boiling point of methane, we perceive the difficulty of practical application, for a standard automobile tank at room temperatures, capacity 15 gallons, would probably lose nearly a quarter of the charge whilst filling.

Dr. Ruhemann refers to the use of cold accumulators, a positive means of power economy. Linde has suggested the use for coke-oven gas separation; we have, I think, improved a device known in other branches of industry for generations by introducing a rapid scavenging between reversals, to avoid gas contamination. By this means, rich coke-oven gas in process of cooling is not deprived of some of its valuable constituents; the lean return gas under low pressure is expanded into the accumulator previously evacuated by pressure release and pump. In the prior stage of benzol recovery the use of the accumulator is permissible by the employment of another refrigerant in place of ammonia, recoverable at a further place in the cooling system. The Kapitza turbine is a considerable improvement on German practice, and precedes any modification of which I am aware.

The octane value of methane transcends 140, which means that a liquid gallon of methane equals in power output a standard gallon of petrol if the compression ratio be raised to 10, possible with most standardized engines. Our resources are vast. Dr. Ivon Graham has reviewed this phase in relation to Colliery Methane. From my own knowledge coke-oven gas is a potential source. It will be obvious that 25 gallons additional of motor spirit per ton of coal is far more profitable than any grid sales for domestic heating. Besides, a mobile liquid gas avoids costly boosters and pipe-lines and enables distribution over a very wide range, without the intervention of the gas distributor.

Liquid oxygen was employed by Linde for explosives in 1900. Mewes had suggested the use of oxygen at a much earlier date. When we investigated liquid oxygen with cotton-filled cartridges in the Cleveland Ironstone Mines twenty years ago as an economical means of displacing gunpowder, the conclusion reached was that evaporation rendered this practice doubtful. The maximum power depends on detonation at a given instant, the sensitivity is high, and the conveyance of dipping flasks from point to point means a continuing loss.

I have directed attention to two phases only which coincide with the activities of ourselves and our collaborators, and now mention our dependence on scientific control at each and every stage in the design and manufacture of plant and equipment for efficient gas separation. The separation of gases, if rightly pursued, infers new industries at a time when we shall be confronted with great difficulty in purchasing our overseas-derived sustenance.

With my collaborators' sanction, we recommend a University Chair for Gases, preferably Cambridge. Our major industries are dependent on more exact knowledge of gases. The Petroleum Institute is, I know, continuously directing research to the utilization of gas from the oil-wells, and Dr. Dunstan of the Anglo-Iranian Company directed attention to this aspect some years ago. I recommend the suggestion to the three Institutes. Cambridge possesses liquefaction plant probably not in use to-day, and within the precincts of the laboratory we find all the gases we require. If this equipment is not available, it is possible that friends owning similar plant will permit its use for research. We are to-day confronted with a fuel shortage. As Mr. Hughes, late Prime Minister of Australia, reminds us, our Air Force is completely dependent on sea-borne supplies of aviation spirit, whilst a huge fuel reservoir wastes under our feet. Stripped to the K ring as we "pass through the valley of adversity," let us "use it as a well," and avoid the just censure of a future generation if we fail to employ in times of need the gases Providence has placed at our disposal.

Mr. G. Baars writes: I have followed with great interest the lecture of Dr. Ruhemann on Tuesday last about the separation of gases and make use of the opportunity given to ask one question regarding the statement that: "A detailed study has been made of the scrubbing column and the process of replacing carbon monoxide with nitrogen by scrubbing the mixture with liquid nitrogen, and a new thermodynamic diagram of nitrogen has been constructed, replacing the faulty Dutch diagram and extending to higher pressures the diagram issued by the American Bureau of Mines."

I should very much appreciate it if Dr. Ruhemann could tell me where I can find the Dutch diagram mentioned and what was wrong in it.

Dr. Ruhemann, in a private reply to Mr. Baars, furnished him with a copy of the paper by I. M. Guask,[9] containing a reference to the Dutch diagram, comparing it with the diagram published by the U.S. Bureau of Mines. He thought that Mr. Baars would be interested to know that Keesom and Houthoff's diagram of ethylene, published in the Leyden Communications in 1931, had also proved to be incorrect.

Mr. Baars, acknowledging the loan of the paper by Gusak, referred to the work by Keesom, which, he felt, had not been sufficiently appreciated by the author.

Dr. Ruhemann replied that he had the greatest respect for the work in this and other fields of Prof. Keesom, with whom he had been in close touch. He had felt bound, however, to point out the errors in these diagrams because of their use by engineers for practical calculations. While he believed that the nitrogen diagram was based on the best available data at the time, in the diagram for ethylene there was an unfortunate slip at low pressures which seriously impaired its value for practical and theoretical purposes. He felt that Mr. Baars would agree that even the greatest scientists occasionally made mistakes, but that this did not detract from their greatness.

Mr. B. C. Oldham wrote directing attention to the last paragraph on page 220, in which reference was made to absorption methods. It occurred to the writer that the term " absorption " might be ambiguous; it did not refer, as some readers might conclude, to absorption of a gas for the purpose of separation, but to the absorption method of refrigeration.

THE EXAMINATION OF ETHYL ALCOHOL AND ALCOHOL BLENDS FOR USE AS MOTOR FUEL.[1]

By S. J. W. Pleeth, B.Sc.[2]

Introduction.

The post-war world will see an increase in the use of home-produced substitute fuels such as alcohol and benzole, in all countries not possessing natural petroleum resources. For this reason it is considered expedient at this intermediate stage to discuss tentative methods for the testing of such materials and their blends with petrol, in so far as these tests differ from the standard methods laid down by the Institute of Petroleum, (I.P.), British Standards Institution (B.S.I.), or the American Society for the Testing of Materials (A.S.T.M.). The present paper deals with the examination of ethyl alcohol and its blends with benzole and petrol as practised in the Central Laboratory of the Cleveland Petroleum Co., an organization with many years experience in marketing a successful and popular alcohol blend. The author wishes to thank the directors of this Company for permission to publish this paper and to acknowledge their aid and encouragement in the early years of testing and development.

PART I.—ETHYL ALCOHOL.

The examination of ethyl alcohol is complicated by the attitude of H.M. Customs and Excise, which lays down certain regulations covering the use of alcohol for motor spirit. These state that ethyl alcohol may be used as a motor fuel only when denatured with 5 per cent. wood spirit, 0·5 per cent. pyridine, and a minimum of 30 per cent. petroleum spirit or benzole, and coloured with an approved red dye-stuff. Where it is blended under bond with amounts of petroleum spirit or benzole exceeding this minimum of 30 per cent. (which is the normal commercial practice) it may be supplied containing only 5 per cent. petroleum spirit or benzole, or even, in exceptional circumstances, with no such admixture, other than the first-mentioned denaturants, wood-spirit and pyridine. This section will deal with ethyl alcohol containing no petroleum spirit or benzole, but reference will be made to the pure material, and that after the addition of the legal denaturants, in which case the Customs nomenclature will be adopted—namely, Power Methylated Spirits Stage 1 (P.M.S.1). It will be apparent that all the standard tests for pure alcohol will be modified by the admixed denaturants.

A. Pure Ethyl Alcohol.

It is suggested that the procedure laid down in the B.S.I. Specification 507–1933 be used, modified as shown.

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[1] Received 7th August, 1942.
[2] Chief Chemist, Cleveland Petroleum Company.

1. British Standard ethyl alcohol shall be clear, colourless, and free from matter in suspension and shall contain no adulterants of any kind.
2. Strength. Omit this paragraph.
3. Miscibility with water. Omit this paragraph.
4. Residue on Evaporation. The material shall not leave more than 0·01 per cent. by weight of non-volatile residue, when tested in the manner described.
5. Acidity. The acidity of the material, other than that due to dissolved carbon dioxide, shall not exceed 0·005 per cent. by weight calculated as sulphuric acid and determined in the manner described.
6. Aldehyde Content. The material shall contain not more than 0·1 per cent. by weight of aldehyde, calculated as acetaldehyde, when tested as described.

B. Power Methylated Spirit Stage 1 (P.M.S.1).

1. *Specific Gravity.*

This determination is usually made with an accurate hydrometer, range 0·790–0·810, length of stem 20 cm., and subdivided so that each small

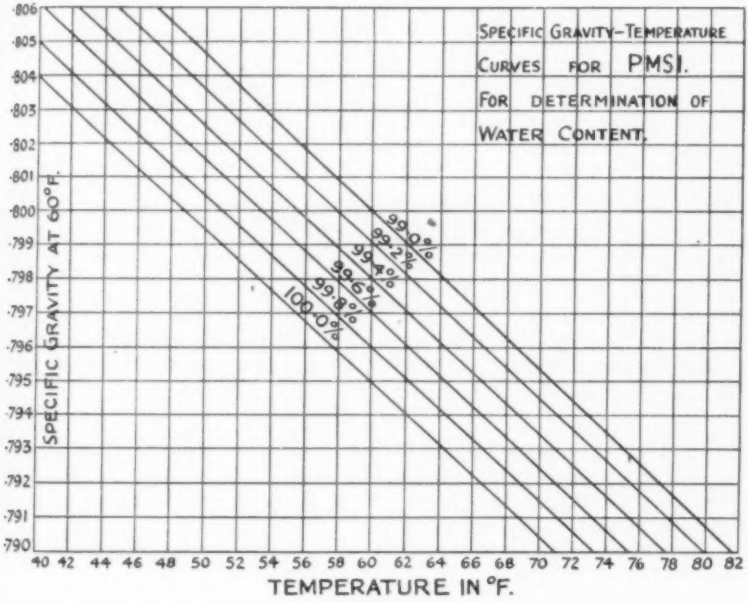

Fig. 1.

division of 0·001 is 10 mm. apart, permitting estimation to 0·0001. The temperature of the alcohol is then determined to 0·5° F., and by calculation, or by the use of a chart similar to that shown in Fig. 1, the specific gravity at 60° F./60° F. may be obtained. This chart may also be used to determine

the water content; it must be remembered that the presence of denaturants slightly alters the standard tables for ethyl alcohol.

Specific Gravity Temperature Correction :

	Pure Ethyl Alcohol.	P.M.S.I.
Per 1° C. . .	0·00086	0·00082
1° F. . .	0·00048	0·00046

Table I gives details of alcohol strengths by volume and weight, together with the corresponding densities of the pure ethyl alcohol, and the specific

TABLE I.

Alcohol, % by vol.	Alcohol. % by wt.	Pure Ethyl Alcohol.		P.M.S.1. S.G. at 60/60° F.
		Density at 20° C.	S.G. at 60/60° F.	
98·0	96·90	0·7988	0·8033	0·8050
98·2	97·15	0·7980	0·8024	0·8040
98·4	97·44	0·7971	0·8014	0·8030
98·6	97·75	0·7962	0·8005	0·8020
98·8	98·07	0·7953	0·7995	0·8010
99·0	98·38	0·7943	0·7985	0·8000
99·2	98·70	0·7933	0·7976	0·7990
99·4	99·02	0·7923	0·7966	0·7980
99·6	99·34	0·7913	0·7956	0·7970
99·8	99·67	0·7903	0·7946	0·7960
100·0	100·00	0·78934 (4)	0·7936 (5)	0·7950 (6)

gravities at 60° F./60° F. for both the pure material and P.M.S.1. If no accurate hydrometer be available, the density may be determined by means of a calibrated pyknometer or bottle, details of which may be found in I.P.—59/42.[1]

2. *Distillation Range.*

For purposes of identification and indication of purity, the distillation range may be determined by the I.P. Method 28/42 [A.S.T.M. : D86–30].[2]

3. *Water Content.*

(*a*) The determination of small concentrations of water in ethyl alcohol is rapidly obtained by the method of Crismer.[7] This method depends on the determination of the critical solution temperature (C.S.T.) of mixtures of aqueous alcohol and kerosine.

Apparatus. (See Fig. 2).

1. Unsilvered Dewar Flask.
2. 6″ × 1″ Pyrex Test-tube.
3. Thermometer calibrated from 0° to 20° C. in 0·1°.

Method.—Pure anhydrous ethyl alcohol is prepared by refluxing A.R. ethyl alcohol in contact with calcium wire for 2 hours. An approximate C.S.T. is then determined with the kerosine available by mixing 10 ml. of

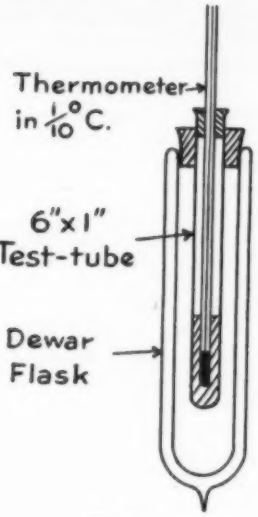
Thermometer
in 1/10° C.
6"x1"
Test-tube
Dewar
Flask

FIG. 2.

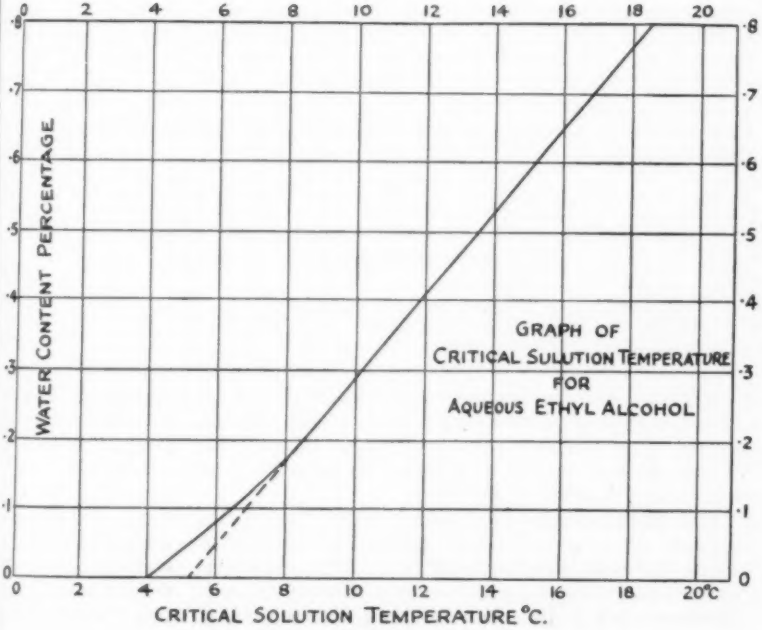
WATER CONTENT PERCENTAGE
GRAPH OF
CRITICAL SULUTION TEMPERATURE
FOR
AQUEOUS ETHYL ALCOHOL
CRITICAL SOLUTION TEMPERATURE °C.
0
2
4
6
8
10
12
14
16
18
20
·1
·2
·3
·4
·5
·6
·7
·8

FIG. 3.

each liquid in the test-tube and warming or cooling until a clear solution is obtained; and by adjustment of temperature until a cloudiness is seen. This C.S.T. is then adjusted to come within the lower range of the thermometer scale by replacing part of the kerosine with petroleum ether. The suitable blend of kerosine and petroleum ether, carefully dried over $CaCl_2$, is prepared in bulk sufficient for the remainder of the determination.

The next stage is the preparation of a C.S.T. graph, similar to that shown (Fig. 3). An aqueous alcohol solution is prepared by adding a weighed quantity of water (about 5 gr.) to a weighed quantity of the anhydrous alcohol (about 95 gr.). Then, by suitable blending of weighed amounts of the anhydrous and aqueous alcohol, solutions containing accurately known quantities of water may be easily obtained. 10 ml. of aqueous alcohol and anhydrous kerosine-petroleum ether are each pipetted into the pyrex test-tube, the thermometer inserted so that the bulb is covered by the liquids and the whole chilled until separation is observed. The tube is carefully wiped and inserted into the Dewar flask. The rise in temperature should be sufficiently slow to enable the C.S.T. to be determined within 0·02° C. (This corresponds to an accuracy of 0·001 per cent. in the water content.) Sufficient determinations are made to enable a reasonable curve to be plotted. The graph is a straight line for water contents above 0·2 per cent., but an appreciable deviation is observed below this figure.

The final stage is the actual determination of the water content of the sample in question. This proceeds as in the preparation of the C.S.T. curve, care being taken that both liquids are filtered. From the C.S.T. obtained, the water content of the aqueous alcohol may be read with an accuracy approaching 0·01 per cent.

(*b*) An excellent alternative method for the determination of water contents is that due to Botset.[8] It may be preferred to that of Crismer, as it requires no elaborate apparatus and is suitable for a greater range of water contents.

Materials Required.

1. Absolute alcohol of known strength.
2. Anhydrous carbon tetrachloride A.R.
3. Two 10-ml. pipettes.
4. One 10-ml. burette, graduated 0·05 ml.
5. 6″ × 1″ hard glass test-tube.
6. Thermometer in °F. (or °C.).

Method. Into the test-tube are pipetted 10 ml. absolute alcohol and 10 ml. anhydrous carbon tetrachloride. The test-tube is closed with a tightly-fitting cork in which is inserted the thermometer, which is adjusted so that the bulb is entirely immersed in the liquid. The test-tube is then cooled to approximately 60° F.

From the burette distilled water is added, drop by drop, until a cloudiness appears, the temperature being maintained at 60° F. by immersion in ice-water at intervals. The test-tube is then warmed by contact with the hand, until the solution becomes clear, when another drop of water is added. This procedure is continued until two burette readings are obtained, one giving a cloud point below 68° F., and one above, so that by interpolation

an exact titration figure for the cloud-point may be obtained. A result accurate to 0·02 ml. of water is possible by this means.

This method is then repeated with ethyl alcohol containing known amounts of water, until a calibration curve is obtained, similar to Fig. 4. In general, absolute ethyl alcohol requires a titration figure of 2·0 ml. at 68° F. (25° C.), although denaturants slightly affect this figure. Furthermore, each 1° F. is equivalent to 0·01 ml. of water in causing separation.

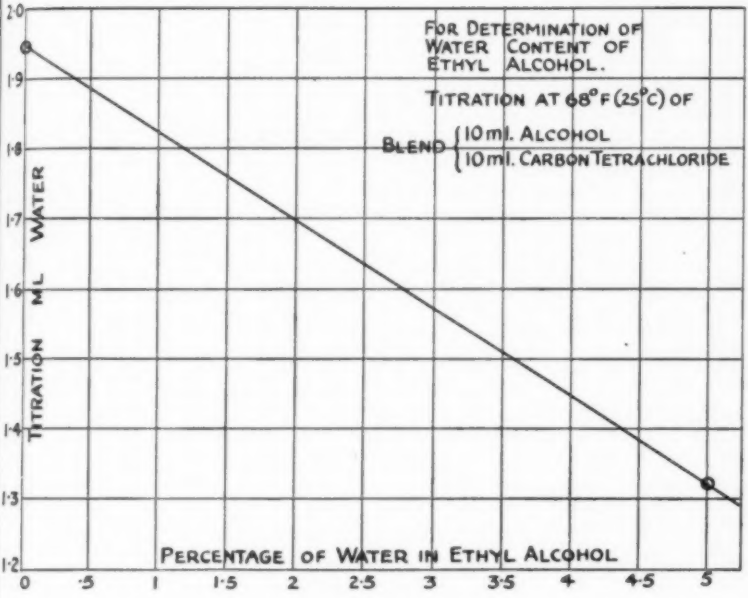

FIG. 4.

When we come to examine an unknown alcohol sample, it is titrated in the same way as indicated above and the water content read off directly. For instance, a titration of 1·75 at 68° F. would correspond to a water content of 1·53 per cent.

The accuracy of the method is within ± 2 per cent. of the stated water content.

PART 2.—ALCOHOL BLENDS.

The examination of motor fuels containing alcohol differs but little from that of other motor fuels, and in the following section only the special tests will be given in full. It is understood that the complete details of the normal tests may be found in the standard tests issued by the Institute of Petroleum, American Society for Testing Materials (A.S.T.M.), etc.

1. *Specific Gravity.*

This property is usually determined by hydrometer and recorded at 60° F./60° F., in accordance with the I.P. Method 59/42. The correction to be applied to the value at a temperature other than 60° F., to reduce to that standard temperature, is usually taken as 0·00048 per 1° F. This value is approximate and applies to blends containing up to 20 per cent. alcohol and 20 per cent. benzole. If the fuel contains higher percentages

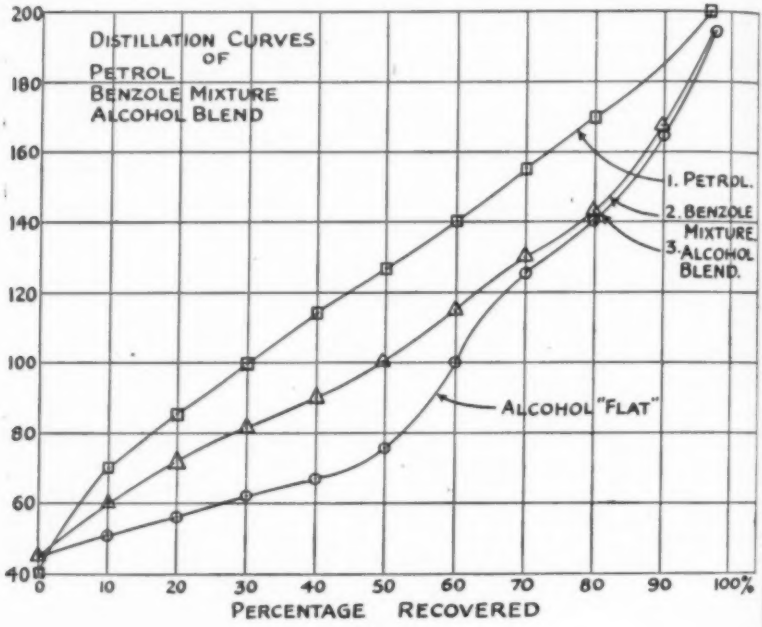

FIG. 5.

of these substances, the appropriate correction must be calculated from the values for the constituents, which are as follows :—

Petrol,* Sp. Gr. below 0·740 . . .	0·00048 per °F.
„ „ „ above 0·740 . . .	0·00044 „ °F.
Alcohol	0·00046 „ °F.
Benzole	0·00056 „ °F.

* For fuller details see I.P. Standard Methods, p. 267.

2. *Distillation.*

The standard method is I.P.—28/42 or A.S.T.M. D86–30. Owing to the formation of azeotropes during the distillation, a typical feature of the distillation curve is the "alcohol flat" (see Fig. 5, Curve 9). This affects the rate of distillation, for when the temperature reaches about 80° C.,

the rate falls, while the temperature rises rapidly to about 110° C., and then both the rise in temperature and the distillation rate proceed normally. It is generally accepted that the flame height should not be adjusted during this period, to maintain the standard rate of distillation.

3. *Vapour Pressure.*

In the standard method for the determination of the Vapour Pressure of Motor Spirits by the Reid method (I.P.—69/42, A.S.T.M.: D323–32T) certain precautions and modifications are necessary when examining blends containing ethyl alcohol. The present note may be found useful to new workers in this field, in consequence of the growing importance of alcohol blends.

The first precaution is obvious: the sample cannot be obtained by water displacement, and the gasoline chamber may be filled either by direct immersion into the sample to be tested, or by pouring, if the temperature be low enough, or by siphon, the normal method for laboratory use.

The second precaution is less obvious, and may easily be overlooked. The standard method states that the air-chamber shall be rinsed with water before use and the temperature of the air within the chamber taken. When now the spirit is introduced, the bomb assembled, and the whole immersed in a bath at the standard temperature of 100° F., the rise in pressure is due to the increase in vapour pressure of the gasoline and the water (considered as saturated by providing excess) and by the normal pressure increase of air. To obtain the required vapour pressure of the gasoline, a correction is applied to the gauge reading corresponding to the two other factors introduced. This is given by the standard correction

$$\frac{(P_a - P_t)(t - 100)}{460 + t} - (P_{100} - P_t)$$

where t = initial air-chamber temperature, ° F.
P_t = vapour pressure of water in lb. per sq. in. at t° F.
P_{100} = vapour pressure of water in lb. per sq. in. at 100° F.
P_a = normal barometric pressure in lb. per sq. in.

In the author's laboratory it has been observed that the amount of water left in the bomb after rinsing is usually sufficient to cause separation of the alcohol blend into the two phases: aqueous alcohol and petroleum spirit.

The standard correction no longer applies, for there is no free water in the bomb. In any case, the recorded vapour pressure is erroneous, for, by Raoult's Law, the total vapour pressure of immiscible liquids is the sum of their partial pressures, and would lie between the values for aqueous alcohol and petroleum spirit; whereas it is well known that alcohol and petroleum hydrocarbons give azeotropes of higher vapour pressure than either of their constituents.

We have therefore taken the liberty of modifying the standard method when testing alcohol blends by using a dry bomb, by rinsing with alcohol or acetone and blowing with air; an initial air temperature is obtained, the gasoline chamber filled by siphoning, and the method proceeds as before.

The correction factor to be applied in this case ignores the water-vapour factor, as we assume that the pressure of the water vapour in the air at

the commencement of the test increases with temperature to the same extent as does the air. The factor now becomes

$$\frac{P_a(t - 100)}{460 + t}$$

or to a close approximation

$$0{\cdot}03(t - 100) \text{ lb.}$$

Using this method, the true vapour pressure of alcohol blends is obtained, and the phenomenon of the enhanced vapour pressure of azeotropes of ethyl alcohol, benzole, and petroleum spirit readily observed.

One final point : it has often been stated, especially in the American journals, that alcohol motor-spirit blends cause greater vapour locking in an automobile than normal petroleum-spirit fuels of the same Reid Vapour Pressure. We have never found this difficulty to arise in practice on English roads, and this may be due to the less severe temperature conditions that apply here. An alternative explanation might be obtained in the light of the present paper.

Failure to observe the precautions outlined above would result in a depreciation of vapour pressure of alcohol motor spirits of several lb. per sq. in. Thus an alcohol motor spirit of true Reid Vapour Pressure of 10 lb. might be recorded as only 8 lb. This fuel would then be tested in an automobile against a petroleum motor spirit of only 8 lb. vapour pressure, and would, of course, reveal an enhanced tendency to vapour lock. Had it been tested against its equivalent—a petroleum motor spirit of 10 lb. vapour pressure—the opposite result would have been recorded, as our own road tests have shown, a result that confirms theoretical considerations.

4. *Water Tolerance.*

There are a number of methods by which this property of alcohol blends may be determined and recorded. That adopted by this laboratory is the amount of water that just causes separation at 60° F., recorded as ml. per gallon (that peculiarly Anglo-Saxon hybrid) or as a percentage.

Apparatus Required.

1. 1-ml. micro-burette (in 0·01 ml.).
2. 50-ml. pipette.
3. 6″ × 1″ hard glass test-tube.
4. Internal scale thermometer 32° F.–100° F.

Method.—30 ml. of the alcohol blend are pipetted into the dry test-tube and closed with a tight-fitting cork, in which is inserted the thermometer, the bottom of which should be about 1 inch from the bottom of the test-tube. (The purpose of the internal scale will be appreciated when one observes the rapidity with which the colour of the normal thermometer scale is removed by the blend; a burnt-in scale will also prevent this occurrence.)

The test-tube is then inserted into an ice-water bath and the temperature of the contents reduced to about 40° F. Water is then added from the micro-burette until the contents become cloudy. It is clarified by warming with the hand, and another 0·01 ml. added, again causing clouding,

which in turn is removed by warming slightly. This is continued until sufficient water is added to cause the contents of the tube to remain cloudy at 60° F. It is always advisable to continue to warm the tube slightly and obtain the exact temperature of clarification. This guards against an accidental admission of excess water, for it is known that 0·01 per cent. water is equivalent to 2° F. (or 0·01 ml. = 4° F.).

The titration is doubled, to record percentage. To convert to ml. per gallon, the percentage is multiplied by the factor 45·5.

Remarks.

Fig. 6 records the results of determinations in the author's laboratory by the above method. The materials used were P.M.S.1, a high-grade acid-washed motor benzole, and a cracked Venezuelan petrol.

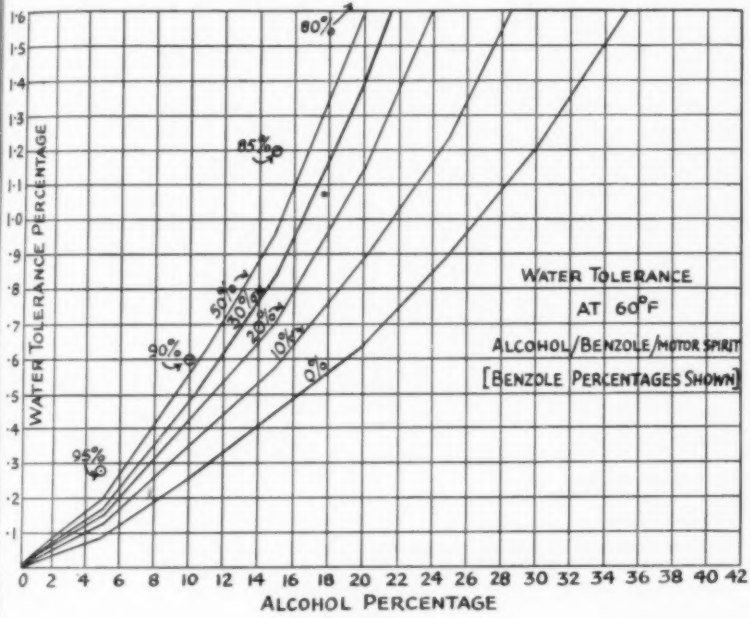

Fig. 6.

Fig. 7 represents these results in a more comprehensive form by means of a triangular graph.

Fig. 8 represents these results in a form complementary to that shown in Fig. 6. It illustrates an empirical formula for the calculation of the water tolerance of petrol blends containing not more than 20 per cent. alcohol and 20 per cent. benzole—that is, within the normal commercial limits.

$$\text{Water Tolerance at } 60^\circ \text{ F.} = \frac{(1{\cdot}2A - 3)(B + 30)}{1000} \text{ per cent.}$$

The full lines record actual results, the dotted calculated by this formula. Within the limits stated the accuracy is experimental (5 per cent. or less).

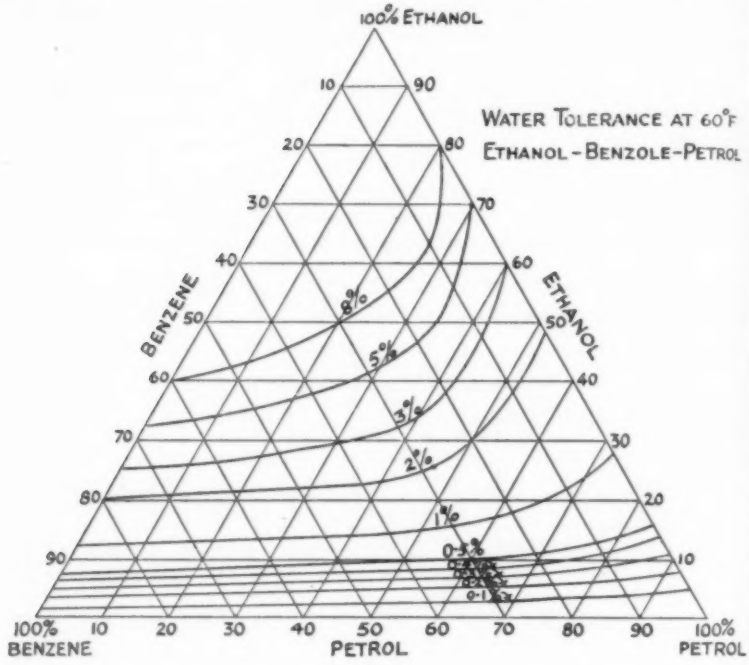

FIG. 7.

5. *Analysis of Constituents.*

1. *Alcohol Content.*

Apparatus.

Glass shaker of following dimensions, and of hard glass :—

Bulb A . . .	volume 250 ml.
Bulb B . . .	,, 80 ml.
Stem CD . . .	,, 20 ml., graduated to 0·1 ml.
Total volume C to E .	,, 100 ml.
Graduations to commence from 0 at C.	
Bulbs A and B . .	pear-shaped.
Bulb A . . .	with neck for cork.
Bulb B . . .	with tap.

Method.—A small volume of brine is sucked through the tap to reach lowest graduation E. 100 ml. of the alcohol blend are pipetted into the vessel, so that it reaches C. 100 ml. of saturated brine are added, the cork

tightly fitted, the vessel inverted and shaken for 5 minutes and allowed to stand vertically. When separation is complete, the brine is run out until

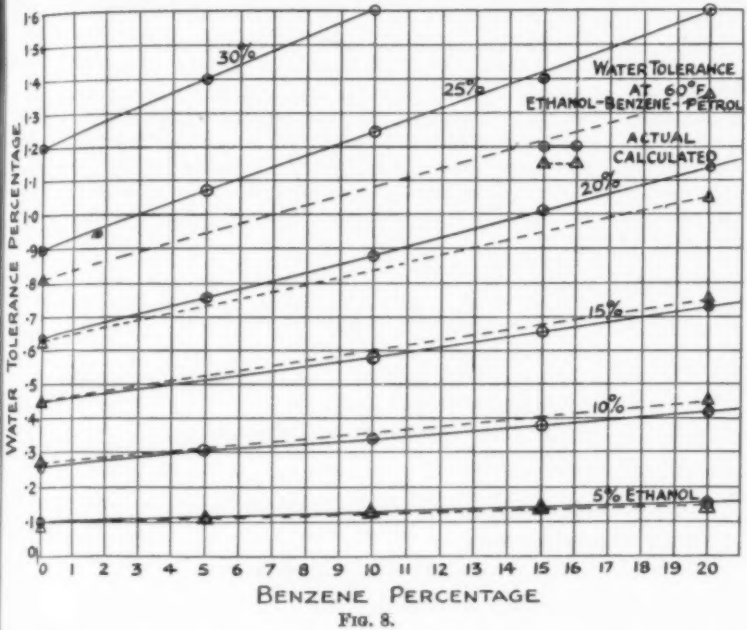

FIG. 8.

the lower level of the petrol reaches graduation E. The vessel is allowed to stand for a few minutes, and the level again adjusted, and this is continued until no further drainage is observed.

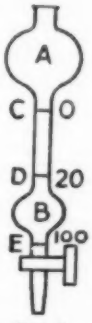

FIG. 9.

The reading of the upper petrol level records directly the percentage of alcohol in the original blend. If the alcohol content is over 20 per cent.,

an alternative vessel is used, similar to that shown, but omitting bulb B, and with the graduated portion extending along the entire stem from C to E, the volume now being only 50 ml., and that volume of alcohol blend used initially.

Whilst most alcohol motor fuels consist of simple mixtures of ethyl alcohol and petrol, other additions are frequently found. Methyl alcohol, for example, is always present, together with pyridine derived from the denaturant. Sometimes it is added to form a definite portion of the alcohol content (cf. German alcohol blends, in which the alcohol portion consists of 2 parts ethyl and 1 part methyl alcohol). If it is desired to estimate the ethyl and methyl alcohols separately, together with acetone, ether, water, and other possible ingredients, a complete examination may be conducted on the following plan :—

(1) *Shake with brine.*

(*a*) *Water Soluble* (*containing the alcohols, acetone, ether, water, etc.*).

(1) Test for acetone.

(*a*) Positive : determine by method (i) or (ii), remove by method (iii) and proceed.

(*b*) Negative : proceed by method (*a*) below.

(2) Test for ether.

(*b*) *Water insoluble* (*petrol, benzole, aniline, etc.*).

(i) Test for nitrogen.

(*a*) positive : estimate aniline, nitro-benzene.

(ii) Test for thiophene (added benzole).

(iii) Extract with 100 per cent. H_2SO_4 and determine aromatics, unsaturateds, and other hydrocarbons.

The most complex blends are to be found in racing fuels, which may contain ethyl and methyl alcohols, acetone, ether, nitro-benzene, aniline, petrol, motor benzole, tetraethyl lead, and water, in addition to many other ingredients, subject to the whims of the driver, mechanic, or designer of the engine. Each blend presents its own analytical problems, which cannot be dealt with fully here. The following notes cover the broad analysis of the main types of alcohol blends.

(*a*) *Ethyl and Methyl Alcohols.* If it is suspected that the motor fuel contains water-soluble materials other than ethyl alcohol, a complete analysis may be made on the brine extract. First, the petrol layer is shaken with a further 50 ml. of brine, and this second extract added to the first. The entire brine extract is then carefully distilled, using a splash-trap and vertical coil condenser (so that no condensate is trapped), until the distillate has a total volume of 95 ml. It is then cooled to 60° F., and water added until it reaches the 100-ml. mark. (A standard 100 ml. graduated flask should be used to collect the distillate.)

The specific gravity of this distillate is accurately determined by means of a 50-g. bottle; from the appropriate tables [9] the methyl and ethyl alcohol strengths are obtained.

The refractive index of this distillate is then measured by means of a Zeiss Immersion Refractometer, an instrument peculiarly adapted to this specific purpose, or by means of a prism refractometer of equal accuracy.

TABLE II.[10]

Immersion Refractometer Readings at 20° C.

Alcohol, % wt.	Methyl Alcohol.	Ethyl Alcohol.	Alcohol, % wt.	Methyl Alcohol.	Ethyl Alcohol.	Alcohol, % wt.	Methyl Alcohol.	Ethyl Alcohol.	Alcohol, % wt.	Methyl Alcohol.	Ethyl Alcohol.
0	14·5	14·5	26	30·2	61·9	52	39·6	91·8	78	27·6	100·9
1	14·8	16·0	27	30·9	63·7	53	39·6	92·4	79	26·8	100·8
2	15·4	17·6	28	31·6	65·5	54	39·5	93·0	80	26·0	100·7
3	16·0	19·1	29	32·2	67·2	55	39·4	93·6	81	25·1	100·6
4	16·6	20·7	30	32·8	69·0	56	39·2	94·1	82	24·3	100·5
5	17·2	22·3	31	33·5	70·4	57	39·0	94·7	83	23·6	100·4
6	17·8	24·1	32	34·1	71·7	58	38·6	95·2	84	22·8	100·3
7	18·4	25·9	33	34·7	73·1	59	38·3	95·7	85	21·8	100·1
8	19·0	27·8	34	35·2	74·4	60	37·9	96·2	86	20·8	99·8
9	19·6	29·6	35	35·8	75·8	61	37·5	96·7	87	19·7	99·5
10	20·2	31·4	36	36·3	76·9	62	37·0	97·1	88	18·6	99·2
11	20·8	33·2	37	36·8	78·0	63	36·5	97·5	89	17·3	98·9
12	21·4	35·0	38	37·3	79·1	64	36·0	98·0	90	16·1	98·6
13	22·0	36·9	39	37·7	80·2	65	35·5	98·3	91	14·9	98·3
14	22·6	38·7	40	38·1	81·3	66	35·0	98·7	92	13·7	97·8
15	23·2	40·5	41	38·4	82·3	67	34·5	99·1	93	12·4	97·2
16	23·9	42·5	42	38·8	83·3	68	34·0	99·4	94	11·0	96·4
17	24·5	44·5	43	39·2	84·2	69	33·5	99·7	95	9·6	95·7
18	25·2	46·5	44	39·3	85·2	70	33·0	100·0	96	8·2	94·9
19	25·8	48·5	45	39·4	86·2	71	32·3	100·2	97	6·7	94·0
20	26·5	50·5	46	39·5	87·0	72	31·7	100·4	98	5·1	93·0
21	27·1	52·4	47	39·6	87·8	73	31·1	100·6	99	3·5	92·0
22	27·8	54·3	48	39·7	88·7	74	30·4	100·8	100	2·0	91·0
23	28·4	56·3	49	39·8	89·5	75	29·7	101·0			
24	29·1	58·2	50	39·8	90·3	76	29·0	101·0			
25	29·7	60·1	51	39·7	91·1	77	28·3	100·9			

TABLE III.[11]

Conversion from Zeiss Refractometer Readings to Refractive Indices.

Scale Divisions.	Refractive Index.	Scale Divisions.	Refractive Index.	Scale Divisions.	Refractive Index.	Scale Divisions.	Refractive Index.
− 5	1·32539	25	1·33704	55	1·34836	85	1·35931
0	1·32736	30	1·33895	60	1·35021	90	1·36110
+ 5	1·32931	35	1·34085	65	1·35205	95	1·36287
+10	1·33126	40	1·34274	70	1·35388	100	1·36464
+15	1·33320	45	1·34463	75	1·35570	105	1·36640
+20	1·33513	50	1·34650	80	1·35751		

The Zeiss Refractometer has a limited range of refractive index readings (with Prism I) ranging from 1·325 to 1·366, recorded on an arbitrary scale ranging from 0 to 100. This scale corresponds to the complete range of values found in aqueous ethyl and methyl alcohols, and permits a rapid determination of their relative proportion to be obtained. In the absence of such an instrument, the normal refractive index must be converted to Zeiss Refractometer readings by means of Table III.

The method is best explained by means of an actual example.[10] Let us suppose that the specific gravity of the unknown solution is 0·97917 at 60°/60° F. From the standard tables, this corresponds to 13·70 per cent. ethyl or 12·83 per cent. methyl alcohol.

From Table II we observe that the Refractometer reading for 13·70 per cent. ethyl alcohol is 38·16 and for 13·70 per cent. methyl alcohol 22·42. The actual refractometer reading of the unknown solution is (say) 30·0. Then by applying the simple Rule of Three, we have

$$\frac{38{\cdot}16 - 30{\cdot}0}{38{\cdot}16 - 22{\cdot}42} \times 100 = 51{\cdot}8 \text{ per cent.},$$

i.e., 51·8 per cent. of the alcohol in the solution is methyl alcohol.

Now the total weight of mixed alcohols in the solution is given by $(12{\cdot}83 \times 0{\cdot}518) + 13{\cdot}70\ (1 - 0{\cdot}518) = 13{\cdot}25$ per cent., of which $13{\cdot}25 \times 0{\cdot}518 = 6{\cdot}86$ per cent. is methyl alcohol, and $13{\cdot}25 \times (1 - 0{\cdot}518) = 6{\cdot}39$ per cent. is ethyl alcohol.

It must be understood that this method is applicable only in the absence of appreciable amounts of other water-soluble materials that may affect both the gravity and refractive index of the distillate, and therefore invalidate the deductions made. In case of doubt detailed tests must be made for other constituents, and the method is briefly as follows.

(*b*) *Acetone.* The presence of acetone in addition to the alcohols may be confirmed by the following test : to the aqueous solution ammonia is added until it is just alkaline and avoiding excess. A solution of iodine in potassium iodide is then added, drop by drop, until a small amount of black precipitate (NI_3) is formed. The solution is then gently warmed until the precipitate disappears. The presence of acetone is shown by the formation of iodoform (crystals or odour). Under these conditions of test ethyl alcohol does not produce iodoform.

If acetone is found present, its determination may be obtained by one of two methods, depending on the presence or absence of methyl alcohol.

(i) If methyl alcohol is absent, proceed by the method of Rakshit and Messenger [12] or Marasco.[13]

(ii) If methyl alcohol is present, proceed by method of Sunwalla and Katti.[14]

(iii) If acetone is present, it must be removed from the brine solution before proceeding with the determination of the alcohols. This is accomplished by adding to 50 ml. brine washings 3 ml. benzaldehyde to each 1 ml. acetone, and 1 g. KOH per 10 ml. liquid. Water is added and the whole refluxed for 30 minutes. It is then distilled, using a splash-trap until all alcohol has been removed. The distillate is saturated with salt and extracted twice with benzole and twice with petroleum ether. The brine washings are then distilled and the method proceeds as in (*a*).

For more complete details of the tests for, and determination of, other possible water-soluble ingredients, such as ether, pyridine, etc., refer to Simmonds' " Alcohol " or other standard work on quantitative analysis.

(*c*) *Water.* Water is best determined by difference, after the determination of other constituents, with a final check by its Water Tolerance.

2. *Petrol.*

That portion of the alcohol blend insoluble in brine may be more fully examined to determine the nature of the petrol used and whether benzole has been added. The procedure follows the customary lines : specific

gravity, distillation range, and bromine value (for unsaturated hydrocarbons) will establish the general type of the petrol and give some indication of the presence of benzene. Although there is no specific test for benzene, most motor benzole contains thiophene (C_4H_4S), and this may be detected by the following test.

(*a*) *Test for Thiophene.* In a white porcelain dish pour a few c.c. of concentrated H_2SO_4. Gently run petrol upon the surface by means of a pipette, taking care not to disturb the interface. Sprinkle a few specks of isatin upon the surface. A blue colour indicates thiophene; normally, yellows and browns develop. This test is not very satisfactory, and does not always reveal the presence of thiophene. It may be assumed that if the test is positive, the petrol contains added motor benzole.

If the thiophene test is negative, or if it be deemed of insufficient value as an indication of added benzole, the petrol may be examined more fully by extraction with concentrated H_2SO_4, on the lines laid down in the I.P. tentative method, and the total aromatics determined by the aniline point. As far as the composition of the fuel is concerned, it matters little whether the aromatics are derived from the petrol itself or from added motor benzole; the results are indistinguishable.

Crank-case Dilution.

In the standard method for the determination of crank-case dilution (A.S.T.M. D322–35 and I.P.—23/42 (T.)), only the petrol portion is caught and measured. The alcohol, if any, remains in solution in the water used, and escapes detection.

It is preferable, therefore, in this case to revert to the original method of direct steam distillation of the crank-case oil, capturing the petrol diluent in the usual siphon trap and collecting all the condensed water. When the steam distillation is completed, the entire distillate is saturated with salt, the petrol part extracted by two or three washings with petroleum ether, and the aqueous portion distilled to 95 ml. in a standard 100-ml. flask. Water is added to the mark and the specific gravity determined. Reference to the standard alcohol tables (see Simmonds' "Alcohol"[9]) enables the alcohol content to be calculated, and from that the alcohol content of the diluent.

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